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(54) Water-soluble quaternary polyammonium salts, process for preparing them, and their use.

(57) The invention concerns new water-soluble quaternary polyammonium salts based on unsaturated quaternary ammonium salts and, in particular, poly(dimethyldiallyl-ammonium chloride) (poly-DMDAAC), comprising 10 to 100 percent by weight of highly branched polymer with a molecular weight > 100,000, with 97.0 to 99.9% monomer and 0.1 to 3.0% mole-% of a crosslinking comonomer and linear poly-DMDAAC. These polyammonium salts are highly branched and have only a very low proportion of short-chain products. They are suitable for use advantageously, individually or in combination with other water-soluble anionic and/or neutral polyelectrolytes as aids for separation processes, such as flocculating agents in wastewater treatment and for production of conductive layers.

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The polyammonium salts according to the invention are prepared by copolymerizing unsaturated quaternary ammonium salts with crosslinking comonomers, the crosslinking comonomer or a mixture of crosslinking comonomers being added during the progress of the homopolymerization or copolymerization of the unsaturated quaternary ammonium salt after conversions of 25 to 90%, in proportions of 0.1 to 3.0 mole-%, based on the unsaturated quaternary ammonium salt.

Water-soluble quaternary polyammonium salts, process for preparing them, and their use

The invention concerns new quaternary polyammonium salts which can be used advantageously either alone or in combination with water-soluble anionic and/or neutral polyelectrolytes as an aid in separation processes, e.g., as flocculating agents in wastewater treatment or as demulsifying agents in breaking of oil/water emulsions, as well as for preparation of conductive layers, such as a conductive layer in production of electrophotography papers.

It is known that water-soluble quaternary polyammonium salts having the structure of linear polymeric pyrrolidinium compounds can be prepared by radical-initiated solution polymerization of dialkyldiallylammonium salts in water, using various initiator systems. Examples of such processes are known from US Patent 3,288,770 or DD-A 127 729.

Copolymerizations with crosslinking comonomers are done to get particular product properties, or to prepare polymers with higher molecular weights. That is done by making mixtures of diallylammonium salts and a crosslinking comonomer, such as a dicarboxylic acid diallyl ester (DD-A 127 729, 128 189, 128 247) or triallylamine hydrochloride or tetraallylammonium chloride (FR-B 1 494 438, US Patent 3,544,318), mixing them with an initiator, and polymerizing. In all the known variations of the polymerization of diallylammonium salts alone or with any comonomers, though, the products are polymers containing a not-insignificant proportion of short-chain products. The relative viscosity in solution, η_{rel} , is a measure of the molecular weight and, thus, of the chain length. In all the known processes for producing polymeric ammonium salts, η_{rel} decreases with increasing conversion. That is, short-chain products are produced increasingly with increasing conversion. That situation is a disadvantage for many applications of water-soluble polyammonium salts if the particular application properties are due to the higher-molecular-weight components of mixtures of polymer molecules with polymer chains of different lengths.

For many applications, e.g., as conductive resins in production of electrophotography paper, the specific technical properties are better if the polyammonium salts have high molecular weights and are water-soluble, but highly branched; that is, if they have a high proportion of crosslinking comonomers (cf. DD-A 127 729, 128 189, 128 247 and US Patent 3,544,318).

To be sure, several process variations are known, e.g., from US Patent 3,544,318, or from J.E. Morgan, M.A. Yorke, J.E. Boothe, "Ions in Polymers," *Advances in Chemistry, Series 187*, p. 240, for preparing polymers with higher average molecular weights from quaternary diallylammonium salts with crosslinking comonomers; but the proportion of crosslinking comonomers is low, so that the degree of branching is relatively low, and also not-inconsiderable proportions of short-chain polymeric molecules necessarily occur. It is mentioned, to be sure, in DD-A 127 729, 128 189 and 128 247, that up to 5 mole-% of the comonomer is used in polymerization of dimethyldiallylammonium chloride (DMAAC) with dicarboxylic acid diallyl esters, for example. This high proportion is not usable, though, because the comonomers are only very slightly water-soluble and therefore do not react completely.

It is known from the literature that if the proportion of crosslinking comonomer is too high, the polymer obtained is partially or completely crosslinked (gelled), and thus is insoluble and unsuitable for any application as a soluble polymer. See, for instance, B. Vollmert, *Grundriss der makromolekularen Chemie* [Outline of Macromolecular Chemistry], Springer-Verlag, Berlin, 1962, p. 196. It is generally the case that when mixtures of a monomer and 0.1% by weight of a crosslinking polymer are polymerized, the polymer, initially completely soluble, transforms to a state of limited swellability (Houben-Weyl, *Methoden der organischen Chemie* [Methods of Organic Chemistry], 4th Edition, Georg-Thieme Verlag, Stuttgart, 1961, Volume 14/1, p. 1078). In solution polymerization of mixtures of dimethyldiallylammonium chloride (DMAAC) with the crosslinking comonomer methyltriallylammonium chloride (MTAAC) in water, insoluble gels were produced even with only 0.035 mole-% MTAAC. Somewhat higher proportions of MTAAC can be used in copolymerization with DMAAC to produce soluble polymers only if the polymerization is done by the substantially more expensive procedure of inverse emulsion polymerization. From the literature on studies of applications, it can be found that the limit for forming completely soluble polymers must be set at 0.5 mole-% MTAAC (J.E. Morgan, M.A. Yorke, J.E. Boothe, "Ions in Polymers," *Advances in Chemistry, Series 187*, p. 240). But even these polymers contain a high proportion of short-chain products. Formation of insoluble crosslinked polymers is a critical problem in production management for production of soluble polymers. The potential for forming such polymers increases as conversion increases. At the same time, polymers which contain only a small proportion of gel are less

suitable for many applications, and cause problems in applications technology. If one wishes to produce a soluble branched polymer by polymerization in the relatively simple and cost-effective process of solution polymerization, one is forced to work with minimal concentrations of crosslinking comonomer.

In the known processes for copolymerizing quaternary diallylammonium salts with crosslinking comonomer to form soluble polymers, the comonomer used is mixed with the monomer at the beginning of the polymerization (DD-A 127 729, 128 189, 128 247, US Patent 3,544,318, J.E. Morgan, M.A. Yorke, J.E. Boothe, "Ions in Polymers," Advances in Chemistry, Series 187, p. 240). The higher the proportion of crosslinking comonomer in relation to the monomer, the higher the proportion of insoluble crosslinked polymer that is formed. Therefore a polymerization process to produce soluble polymers is forced to work with very low proportions of crosslinking comonomers. That does indeed give polymers with increased molecular weight, but there is only limited ability to adjust the degree of branching. It is generally too low, and the proportion of short-chain polymers is too high. Furthermore, the industrial safety of the polymerization process is not adequately assured.

It is the objective of the invention to present an industrially safe and economically favorable process for producing and using water-soluble quaternary polyammonium salts using unsaturated quaternary ammonium salts and especially DMDAAC as the monomer, consisting of highly branched high-molecular-weight polymers with a low proportion of short-chain products, mixed, if desired, with linear polyammonium salts based on the same or a different unsaturated quaternary ammonium salt, in which the formation of gel components or complete gelling is avoided under all circumstances.

The objective has been attained according to the claim.

The water-soluble quaternary polyammonium salts according to the invention are polymers based on unsaturated quaternary ammonium salts, and, in particular, on dimethyldiallylammonium chloride (DMDAAC) and a crosslinking comonomer. They can be obtained by a radical-initiated polymerization of the unsaturated quaternary ammonium salts with the crosslinking comonomer, in which the crosslinking comonomer or a mixture of crosslinking comonomers is added during the progress of the homopolymerization or copolymerization of the unsaturated quaternary ammonium salt, after conversions of 25 to 90%, in proportions of 0.1 to 3.0 mole-%, based on the unsaturated quaternary ammonium salt.

The polyammonium salts according to the invention are preferably characterized in that they comprise

A) 10 to 100% by weight of a highly branched polymer having a molecular weight $> 100,000$ with 97.0 to 99.9 mole-% monomer units derived from unsaturated quaternary ammonium salt and correspondingly 0.1 to 3.0 mole-% comonomer units of one or more crosslinking comonomers, in which the total proportions of the monomer units of unsaturated quaternary ammonium salt and comonomer units total 100 mole-%,

and

B) 0 to 90% by weight of linear homopolymer of the unsaturated quaternary ammonium salt, in which the branching density of the highly branched polyammonium salts A) is 1 to 25 branch points per 100 monomer units of the quaternary ammonium salt, and the proportion of molecules with $[\eta]$ is from < 0.6 to 5% by weight.

The process according to the invention for producing the water-soluble polyammonium salts defined above is based on its general concept of the radical-initiated polymerization of an unsaturated quaternary ammonium salt and especially of DMDAAC with one or more crosslinking comonomers, and is characterized by the fact that the crosslinking comonomer or a mixture of crosslinking comonomers is added to the polymerization system during the progress of the homopolymerization or copolymerization of the unsaturated quaternary ammonium salt after conversions of 25 to 90%, in proportions of 0.1 to 3.0 mole-%.

According to one preferred embodiment, the polymerization is carried out in aqueous solution containing 30 to 70% by weight of monomer and at temperatures of 18 to 65 °C using a suitable initiator, an initiator system, or suitable initiator combinations.

Dimethyldiallylammonium salts, vinylpyridinium salts, quaternary esters and quaternary amides of acrylic acid and/or methacrylic acid, and appropriate mixtures of these ammonium salts, are particularly suitable as unsaturated quaternary ammonium salts. Dimethyldiallylammonium chloride is preferred as the unsaturated quaternary ammonium salt, both for the proportion of highly branched polyammonium salts and for the proportion of linear polyammonium salts.

Because of the smaller proportion of short-chain polymers from the same input of monomer, a higher yield of substance usable in the industrial application is attained.

The process concept according to the invention yields new water-soluble quaternary polyammonium salts comprising highly branched polymers having a mean molecular weight $> 100,000$ with 97.0 to 99.9 mole-% units of the unsaturated quaternary ammonium salt and correspondingly 0.1 to 3.0 mole-% of one or more crosslinking comonomers from copolymerization of the unsaturated quaternary ammonium salt, particularly DMDAAC, with crosslinking comonomer according to a special process. The total amount of units of the unsaturated quaternary ammonium salt and of the copolymer units is 100 mole-%, and the polymer contains from 0 to 90% by weight of linear quaternary polyammonium salt.

Suitable crosslinking comonomers include alkyltriallylammonium salts with alkyl groups having 1 to 3 carbon atoms, tetraallylammonium salts, tetraallylalkylene diamine salts, triallylamine salts, and methylene-bis(acrylamide).

The highly branched polyammonium salts and their mixtures with linear polyammonium salts are completely water-soluble and free of gels. The branched structure can be demonstrated by light scattering in the known manner. The mean branching number per macromolecule, or the branch density, can be determined by the method of Zimm and Stockmayer (*Journal of Chemical Physics* **17** (1949), p. 1301-1314). In the case of DMDAAC, for example, it was determined that there are from 1 to 25 branching points per 100 DMDAAC units.

In contrast to the linear, or previously known slightly branched polymers, which contain a high proportion of short-chain products, the new highly branched polyammonium salts are also characterized by their insolubility in methanol. Another critical difference between the new highly branched polyammonium salts and the known linear polyammonium salts or the previously known slightly branched polymers, with which the crosslinking agent was added at the beginning of polymerization, and which contain a high proportion of short-chain products, is that the polymers according to the invention have a completely different molecular weight distribution. They have a significantly lower proportion of short-chain products. If the molecular weight distribution is determined by fractional precipitation (Ch. Wandrey, W. Jaeger, G. Reinisch, *Acta Polymerica* **33** (1982), p. 442-444) it is found that the proportion of molecules with $[\eta] < 0.6$ is reduced to values of 0 to 5% from the otherwise average values of 20 to 30%.

In contrast to the previously known polyammonium salts, the highly branched polyammonium salts exhibit better properties for applications. When used as a flocculating agent to separate suspended solids from aqueous suspensions, in sludge dewatering, or in breaking of oil/water emulsions, the same or better separations are attained with smaller quantities. For instance, in flocculation of coal suspensions, the separating power is increased by about 20% for the same amount used, or the amount used can be decreased by about 20% for the same separating power. For emulsion breaking, the residual oil content of the aqueous phase is reduced by an average of 50% with the same amount used, and the light transmission is improved by an average of 25%. The separating effect can be improved even more by combining the polyammonium salts according to the invention with known water-soluble anionic and/or neutral polyelectrolytes.

The process according to the invention is carried out such that the crosslinking comonomer is not added at the beginning, as is usual in the known processes for polymerizing dimethyldiallylammonium chloride in aqueous solution. Instead, it is only added during the progress of the polymerization of the unsaturated quaternary ammonium compound after conversions of at least 25 to at most 90%. It is added as an aqueous solution, diluted, if desired, with monomer solution, in proportions of 0.1 to 3.0 mole-%. It is added all at once, continuously, or distributed over a certain [part] or all of the conversion range stated above. This procedure forms mixtures of linear polyammonium salts which existed before addition of the crosslinking agent and highly branched polyammonium salts. However, if one starts with a solution of the unsaturated quaternary ammonium salt which contains a very low proportion, ≤ 0.03 mole-%, of crosslinking agent, and then continues as described above, only highly branched polyammonium salts are produced.

The copolymerization of the unsaturated ammonium salt with the crosslinking comonomer is done in aqueous solution. In the process, a 30 to 70% solution of the monomer, or such a monomer solution already containing ≤ 0.03 mole-% of crosslinking agent, is used, and the polymerization is initiated with a suitable initiator. After a conversion in the range of 25 to 90% has been attained, the crosslinking comonomer is added in proportions of 0.1 to 3.0 mole-%, based on the monomeric unsaturated ammonium salt. The addition is done once, in portions, or continuously during this conversion range.

Solutions of the comonomer in water or in aqueous monomer solutions are used. With MTAAC as the crosslinker, the monomer solutions containing the crosslinker are prepared in a simple process corresponding to the known process for semicontinuous DMDAAC synthesis. The polymerization temperature is either held constant at 18 to 80 °C, or is gradually raised in this range. To establish a final concentration suitable for the application, the reaction mixture can be diluted during or after the polymerization. Any desired initiators, initiator systems or initiator combinations which start radical polymerization can be used as polymerization initiators. Examples include azo initiators, persulfates, peroxides, or redox systems such as persulfates and sulfites or bisulfites. It is preferable to work with an initiator system of a water-soluble peroxodisulfate, a pH-regulating substance, and a nitrogen base. The polymerization can be carried out under inert gas or in the presence of air oxygen. The final conversion is greater than 95%.

Measurement of the relative solution viscosities showed that when the crosslinking comonomer is added according to the invention, η_{rel} increases as the conversion increases. That is, the formation of short-chain components is greatly reduced (see Example 7).

At the same time, the higher proportion of crosslinking comonomer causes a higher degree of branching. The process according to the invention has the further advantage that it can be operated by an industrially safer process with a higher total proportion of crosslinker without danger of forming gels, so that it not only decisively minimizes the proportion of short-chain polymer but also attains higher molecular weights > 80,000 with increased degree of branching.

This total result is surprising, because it is known that more crosslinked insoluble components are formed with higher proportions of crosslinking comonomer in relation to the monomer. From that knowledge, one would have expected substantial gelling with addition of more crosslinker during the polymerization, even though the proportion of monomer has already decreased.

The quaternary polyammonium salts resulting from the process according to the invention are suitable for all applications in which the application properties depend on the branched and higher-molecular-weight components of the polymer mixture, because of their low proportion of short-chain polymers and their high degree of branching. The same amount of monomer produces a polymer product with a higher proportion of higher-molecular-weight water-soluble polyammonium compounds suitable for the application. That is, the yield of active substance is higher. The concept of the invention is not limited to copolymerization of quaternary diallylammonium salts with crosslinking comonomer. Highly branched water-soluble polymers can also be produced in the same manner by copolymerization of other unsaturated quaternary ammonium salts such as vinylpyridinium salts, or quaternary esters, or amides of acrylic acid and methacrylic acid with crosslinking comonomer.

The highly branched polyammonium salts according to the invention are made as aqueous solutions. They can be converted into pourable soluble powders in a simple thermal process.

The invention is explained in the following by means of example embodiments. All the data about the amounts of monomeric unsaturated quaternary ammonium salts or DMDAAC are in mole-%. The relative viscosity in solution, η_{rel} , was measured with 1% solutions of the previously isolated polymers in 1 N NaCl solution. The polymers were isolated by pouring the polymerized reaction mixture into acetone. The polymers precipitated as white solids. If the polymer solutions contained portions of gelled polymer, they were removed before polymer isolation. The statement A means the number of branches per 100 DMDAAC units. The statement B means the proportion, in percent by weight, of polymer with $[\eta] < 0.6$.

Example embodiments

Example 1

180 g of a 50% aqueous dimethyldiallylammonium chloride (DMDAAC) solution was mixed with 2 mole-% ammonium peroxodisulfate and 2 mole-% ammonium carbonate. The mixture was polymerized for 10 hours with evenly distributed addition of 1 mole-% triethanolamine without nitrogen flushing or other methods to remove oxygen, in a suitable stirring apparatus with moderate stirring. The temperature was

held at 18-22 °C for 8 hours and then raised gradually to 60 °C over a period of 4 hours. After a polymerization time of 6 hours, 1 mole-% methyltriethylammonium chloride (MTAAC) in 50 g 50% aqueous DMDAAC solution was added. After the reaction was complete, the result was a clear polymer solution with a final conversion of 97%; $\eta_{rel} = 3.47$; $A = 18$; $B = 3.6$.

For comparison, a polymerization was carried out under the same conditions, but with the same amount of crosslinker added at the beginning of polymerization. The result was a completely gelled product.

Example 2

A monomer solution was made up according to the procedure of Example 1 after flushing with nitrogen for one hour. The final conversion was 97%; $\eta_{rel} = 3.52$; $A = 20$; $B = 3.3$.

The comparison polymerization likewise gave a gelled product.

Example 3

A 50% DMDAAC solution was polymerized as in the procedure of Example 1, except that the crosslinker, MTAAC, was added after 3 hours polymerization time (corresponding to 25% conversion). The result was a clear polymer solution without gel components. The final conversion was 86%; $A = 20$; $B = 4.1$.

Example 4

A 50% DMDAAC solution was polymerized as in the procedure of Example 1, except that the crosslinker, MTAAC, was added after 9 hours polymerization time (corresponding to 75% conversion). The result was a clear polymer solution without gel components. The final conversion was 97%; $A = 5$; $B = 0$.

Example 5

A 50% DMDAAC solution was polymerized, as in the procedure of Example 1, with methyltriethylammonium bromide as the crosslinker. The result was a clear polymer solution without gel components. Final conversion 96%; $\eta_{rel} = 3.35$.

Example 6

A 50% DMDAAC solution was polymerized, as in the procedure of Example 1, with methyltriethylammonium sulfate as the crosslinker. The result was a clear polymer solution without gel components. Final conversion 97%; $\eta_{rel} = 3.48$.

Example 7

A 50% DMDAAC solution was polymerized, as in the procedure of Example 1, with different proportions of MTAAC as the crosslinker. The comonomer used was added either at the beginning of the polymerization or during the course of the polymerization. All the polymerizations without gelling had final conversions greater than 95%. Measurements of η_{rel} were done on the polymers isolated.

Table 1 shows the results. The course of η_{rel} as a function of the conversion was determined for some of the polymerizations listed in Table 1. The figure shows the results. η_{rel} is a measure of the cumulative molecular weight (determined at a particular conversion). Curve I shows a homopolymerization of DMAAC without crosslinker. The molecular weight decreases steadily. That is, as the conversion increases, increasingly shorter chains are formed and the molecular weight distribution becomes broader.

Table 1: Results of polymerizations from Example 7

Polymer No.	MTAAC addition Time	Proportion (mole-%)	η_{rel}	A	B
1	Beginning	0.03	2.30 completely soluble		
2	Beginning	0.10	2.50 Contains some gel		
3	Beginning	0.25	2.65 Contains some gel		
4	Beginning	0.50	Gelling		
5	After 6 hours	0.10	2.70 completely soluble	1	5
6	After 6 hours	0.50	3.17 completely soluble	11	4.5
7	After 6 hours	0.70	3.40 completely soluble	15	4.0
8	After 6 hours	1.00	3.47 completely soluble	18	3.6
9	After 6 hours	1.50	3.52 completely soluble	20	3.0
10	After 6 hours	2.00	Gelling		
11	After 6 hours and after 10 hours each	0.75 1.5	3.82 completely soluble	21	2.0
12	Continuous addition from 6 to 11 hours	2.00	4.25 completely soluble	22	1.0
13	Continuous addition from 6 to 11 hours	3.00	4.50 completely soluble	25	0

Curve II describes a polymerization of DMAAC with 0.03 mole-% MTAAC as the crosslinking comonomer, added at the beginning of polymerization. Here, again, one can see that η_{rel} decreases with increasing conversion and formation of short-chain components with greater broadening of the molecular weight distribution. For Curve III, 0.25 mole-% MTAAC was added after a reaction time of 6 hours. η_{rel} hardly decreases, and production of short-chained polymers is largely suppressed. For Curve IV, 1.5 mole-% MTAAC was added after 6 hours reaction time. For Curve V, 2 mole-% MTAAC was added continuously from 6 to 11 hours of reaction time. In this case, η_{rel} increases. That indicates not only avoidance of formation of short-chain amines, but also further increase of the average molecular weight.

Example 8

A 50% DMDAAC solution was polymerized as in the procedure of Example 1 with different crosslinking comonomers. The crosslinking comonomers were added either at the beginning of polymerization or after a polymerization duration of 6 hours. The maximum proportion of comonomer which could be added without complete gelling was determined. Table 2 presents the results.

Table 2: Maximum proportions of crosslinking comonomer which can be added without gelling.

Polymer number	Comonomer	Addition at beginning of polymerization		Addition after 6 hours of polymerization	
		Maximum (1 mole-%)	η_{rel}	Maximum (1 mole-%)	η_{rel}
1	Tetraallylammonium bromide	0.10	2.35	1.4	3.30
2	Propyltriallylammonium chloride	0.20	2.40	1.7	3.35
3	N,N,N',N'-tetraallylethylenediamine hydrochloride	0.35	2.05	2.2	2.85
4	Triallylamine hydrochloride	0.40	2.20	2.5	3.25
5	Methylene-bis(acrylamide)	0.60	2.10	3.0	3.20
6	MTAAC + Tetraallylammonium bromide in 1:1 molar ratio	0.10	2.38	1.6	3.35

Example 9

A 30% DMDAAC solution was polymerized as in the procedure of Example 1. The product was a clear polymer solution without gel components. The final conversion was 95%.

Example 10

A 70% DMDAAC solution was polymerized as in the procedure of Example 1. The product was a clear polymer solution without gel components. The final conversion was 98%.

Example 11

180 g of a 50% aqueous DMDAAC solution was mixed with 2 mole-% ammonium peroxodisulfate. It was held, without nitrogen flushing, in a suitable stirring apparatus with moderate stirring for 10 hours at 50 °C. After a polymerization time of 4 hours, 1 mole-% MTAAC was added as a 5% aqueous solution. The result was a clear polymer solution without gel components.

Example 12

2000 moles of a 52.3% aqueous DMDAAC solution were heated to 40 °C in an open stirring machine. Then 2 mole-% ammonium persulfate and 2 mole-% ammonium carbonate were added with stirring and strong cooling. After a total of 1 hour, 1 mole-% triethanolamine was added continuously over a period of 10 hours, with the temperature maintained between 18 and 25 °C. After a reaction time of 8 hours, 0.5 mole-% MTAAC was added at once as a 10 mole-% solution of MTAAC in approximately 50% DMDAAC. As the reaction progressed, the temperature rose to 35 °C with the cooling remaining the same. No further temperature rise was found after 11 hours. Then the solution was heated to 60 °C, with addition of water to dilute it to a final concentration of 20%. It was stirred at this temperature until the reaction was neutral. The result was a highly viscous polymer solution without gel components, at a conversion of 97%; $\eta_{rel} = 3.0$.

Example 13

A 52.3% aqueous DMDAAC solution was polymerized as in the procedure of Example 12, but with the difference that 1.25 mole-% MTAAC was added as the crosslinking comonomer in two proportions: 0.75 mole-% after 6 hours of polymerization and 0.5 mole-% after 10 hours of polymerization. The result was a polymer solution without gel components. The final conversion was 98%; $\eta_{rel} = 3.60$.

Example 14

A 52.3% aqueous DMDAAC solution was polymerized as in the procedure of Example 12, but with the difference that 2.0 mole-% MTAAC was added continuously over a period of 5 hours as the crosslinking comonomer, beginning after polymerization for 5 hours (corresponding to a conversion of 40%). The reaction temperature was maintained in the range of 18 to 25 °C for 8 hours. Then the mixture was continuously diluted at 10 °C/hour and stirred at 65 °C until the reaction was neutral [sic]. The result was a polymer solution without gel components. The final conversion was greater than 99%; $\eta_{rel} = 4.15$.

Example 15

Polymers Number 1 and 7 in Table 1 were compared with respect to their flocculating action. That was done by adding 1 mg of Polymer 1 or 7 to a suspension of 2 g kaolin in 1 liter of water and stirring for 4 minutes at 200 rpm, after which the sedimentation rate of the solids was measured. With Polymer No. 1, $v = 5.7$ m/hr; and with Polymer No. 7, by comparison, $v = 12.1$ m/hr.

Example 16

An aqueous DMDAAC solution which already contained 0.03 mole-% MTAACA at the beginning, was polymerized like the procedure of Example 1. The result was a gel-free polymer solution. The final conversion was 97%; $\eta_{rel} = 3.62$.

Example 17

An aqueous DMDAAC solution which already contained 0.025 mole-% MTAACA at the beginning, was polymerized as in the procedure of Example 13. The result was a gel-free polymer solution. Final conversion 98%; $\eta_{rel} = 3.65$.

Example 18

1 mole of DMDAAC, as a 50% aqueous solution, was brought to 80 °C in a stirring apparatus. Then a total of 10^{-2} mole/liter azo-bis-isobutyronitrile dissolved in 20 ml methanol was added over 10 hours as the initiator. Then the solution was stirred another 90 minutes at 80 °C. After a reaction time of 2 hours, 0.5 mole-% methyltriethylammonium chloride, dissolved in 25 g of 50% aqueous DMDAAC solution, was added over a period of 7.5 hours. The result was a gel-free polymer solution. Final conversion 98%; $\eta_{rel} = 3.10$.

Example 19

Polymerization was done as in Example 18, at 70 °C, and with the initiator dissolved in dimethylacetamide. The result was a gel-free polymer solution. Final conversion 96%; $\eta_{rel} = 3.14$.

Example 20

As in the procedure of Example 18, polymerization was done at 80 °C with addition of 2 mole-% ammonium carbonate. The initiator was 2 mole-% ammonium peroxodisulfate, dissolved in 20 ml water. Final conversion: 94%; $\eta_{rel} = 3.06$.

Example 21

1 mole DMDAAC, as a 50% aqueous solution, was placed in a stirring apparatus. It was mixed with 0.01 mole tartaric acid and 0.02 mole sodium metabisulfite and 10^{-4} mole iron ammonium sulfate, and brought to 40 °C. Then 0.02 moles of ammonium peroxodisulfate was added continuously as a 1 molar aqueous solution over 6.5 hours. After 1 hour of reaction time, 0.5 mole-% methyltriethylammonium chloride was added, dissolved in 25 g 50% aqueous DMDAAC solution, over a period of 5 hours. Then the mixture was stirred for another hour at 40 °C. The result was a gel-free polymer solution. Final conversion 97%; $\eta_{rel} = 3.01$. Addition of the iron ammonium sulfate can be omitted if the work is done in old iron equipment from which traces of iron can go into solution during the polymerization.

Example 22

50 g of a 50% aqueous solution of DMDAAC was placed in a stirring apparatus. It was mixed with 0.80 g ammonium persulfate and 0.30 g lithium bromide, and stirred at room temperature for 24 hours. 0.5 mole-% methyltriethylammonium chloride dissolved in 5 g 50% aqueous DMDAAC solution was added over the period of 6 to 18 hours. The result was a gel-free polymer solution.

Example 23

1 mole DMDAAC, as a 50% aqueous solution, was placed in a stirring apparatus and brought to 50 °C. Then it was mixed with 2 mole-% t-butyl peroxyisovalate. After a reaction time of 3 hours, 1 mole-% methyltriethylammonium chloride, dissolved in 25 g of 50% aqueous DMDAAC solution, was added over a period of 10 hours. The reaction was terminated after a total of 18 hours. The result was a gel-free polymer solution. Final conversion 95%; $\eta_{rel} = 3.49$.

Example 24

A used drilling oil emulsion containing 3% oil by volume was mixed intensively for 10 seconds at 20 °C with the creaming agents shown in Table 3, and then stirred for 45 minutes at about 10 rpm for phase separation. Then the light transmission D of the aqueous phase was measured at a layer thickness of 1 cm, and the residual oil content, c_{oil} , was determined.

Table 3:

Polymer number	P o l y m e r		D (%)	Coil (mg/L)
	Type	Amount added (mg/L)		
1	Copolymer of 83% acrylamide and 17% MTMHS according to US Patent 3,691,086	400	72	105
2	Copolymer of 75% acrylamide and 25% dimethyldiallylammonium chloride according to US Patent 3,585,148	400	69	105
3	Cationic polyvinyl alcohol according to US Patent 3,830,735	400	50	119
4	Poly-DMDAAC according to DD-A 226 481	400	81	83
5	Poly-D-v with 0.5 to 3.0 mole-% methyltriiallylammonium chloride	400	94	36

Example 25

A very stable oil emulsion from metal processing (oil content 3.7% by volume, solids content 6.8 g/L), stabilized with nonionic emulsifiers of the fatty alcohol alkylene oxide adduct type and small proportions of an anionic emulsifier of the aliphatic carboxylic acid type was mixed intensively with 200 mg/L of the highly branched polyammonium salt according to the invention and 100 mg/L anionic polyacrylamide at 20 °C. Then the mixture was stirred for 45 minutes at 10 rpm, after which the phases were separated. The light transmission, D, of the aqueous phase, at a thickness of 1 cm, was 94%, and the residual oil content was 41 mg/L.

Claims

1. Water-soluble quaternary polyammonium salt based on unsaturated quaternary ammonium salts and crosslinking comonomers, obtainable by radical-initiated polymerization of the unsaturated quaternary ammonium salt with the crosslinking comonomer, in which the crosslinking comonomer or a mixture of crosslinking comonomers is added during the progress of the polymerization or copolymerization of the unsaturated quaternary ammonium salt after conversions of 25 to 90% at proportions of 0.1 to 3.0 mole-%, based on the unsaturated quaternary ammonium salt.

2. Polyammonium salts according to Claim 1, characterized in that they comprise

A) 10 to 100 percent by weight of a highly branched polymer having a molecular weight > 100,000 with 97.0 to 99.9 mole-% monomer units derived from the unsaturated quaternary ammonium salt and correspondingly 0.1 to 3.0 mole-% comonomer units from one or more crosslinking comonomers, in which the sum of the proportions of the monomer units from the unsaturated quaternary ammonium salt and the comonomer units is 100 mole-%, and

B) 0 to 90% by weight of linear homopolymer of the unsaturated quaternary ammonium salt, in which the degree of branching of the highly branched polyammonium salt A) is 1 to 25 branch points per 100 monomer units of the quaternary ammonium salt, and the proportion of molecules with $[\eta] < 0.6$ is 0 to 5% by weight.

3. Polyammonium salt according to Claim 1 or 2, characterized in that the unsaturated quaternary ammonium salt is a dimethyldiallylammonium salt, a vinylpyridinium salt, a quaternary ester, or a quaternary amide of acrylic acid and/or methacrylic acid, or an appropriate mixtures of these ammonium salts.

4. Polyammonium salt according to one of Claims 1 to 3, characterized in that the unsaturated quaternary ammonium salt is dimethyldiallylammonium chloride (DMAAC) or is derived from corresponding monomer units of DMAAC.

5. Polyammonium salt according to one of Claims 1 to 4, characterized in that the crosslinking comonomer is an alkyltriallylammonium salt with C_{1-3} alkyl groups.

6. Polyammonium salt according to one of Claims 1 to 5, characterized in that the crosslinking comonomer is a tetraallylammonium salt, a tetraallylalkylenediamine salt, a triallylamine salt, and/or methylene-bis-acrylamide.

7. Process for preparing water-soluble quaternary polyammonium salts according to one of Claims 1 to 6 through radically initiated polymerization with one or more crosslinking comonomers, characterized in that the crosslinking comonomer or a mixture of crosslinking comonomers is added in proportions of 0.1 to 3.0 mole-% during the progress of the homopolymerization or copolymerization of the unsaturated quaternary ammonium salt after conversions of 25 to 90%.

8. Process according to Claim 7, characterized in that the polymerization is carried out in aqueous solution with a monomer content of 30 to 70% by weight and at temperatures of 18 to 65 °C, using a suitable initiator, initiator system, or suitable initiator combination.

9. Process according to Claim 7 or 8, characterized in that the crosslinking comonomer or mixture of crosslinking comonomers is added to the DMAAC as an aqueous solution or mixed with aqueous solutions of DMAAC.

10. Process according to one of Claims 5 to 7, characterized in that the crosslinking comonomer or the mixture of crosslinking comonomers is added once, in portions, or continuously within the conversion range of 25 to 90%.

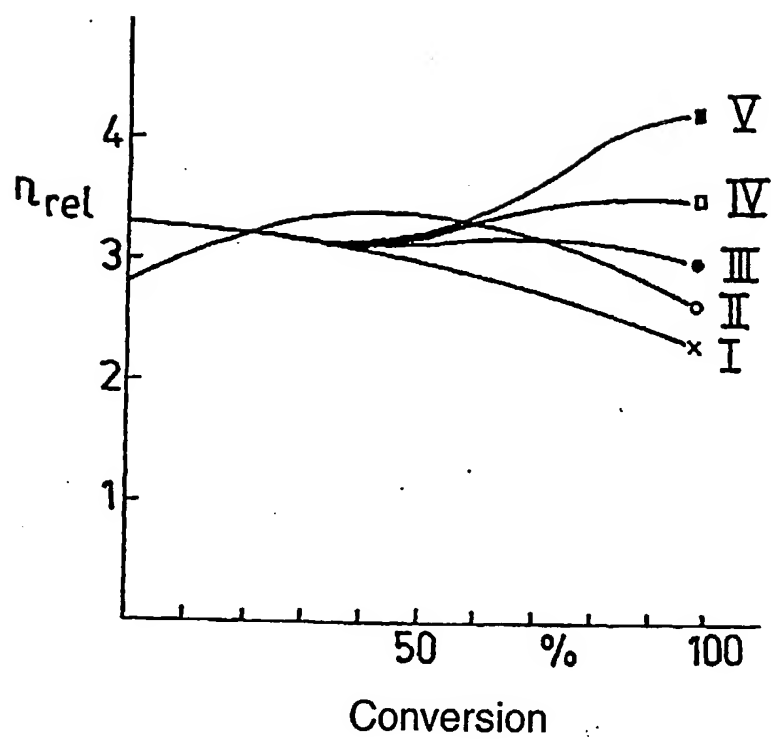
11. Process according to one of Claims 7 to 10, characterized in that dimethyldiallylammonium salts, vinylpyridinium salts, quaternary esters and/or quaternary amides of acrylic acid and/or methacrylic acid, or appropriate mixtures of these quaternary ammonium salts, are used as the unsaturated quaternary ammonium salt.

12. Use of the water-soluble quaternary polyammonium salts according to one of Claims 1 to 6 as an aid for separating processes and in particular as flocculating agents and as demulsifiers for breaking oil/water emulsions.

13. Use of the water-soluble quaternary polyammonium salts according to one of Claims 1 to 6 to prepare electrically conducting layers.

14. Use according to Claim 12 or 13, characterized in that the water-soluble quaternary polyammonium salts are used in combination with polyelectrolytes which are themselves known.

15. Use according to Claim 14, characterized in that anionic and/or neutral polymers are used as the polyelectrolytes.





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EUROPEAN SEARCH REPORT

Application number

EP 87 11 4585

APPLICABLE DOCUMENTS			
Category	Characterization of the documents, with statement, as required, of the critical parts	Concerns Claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ⁴)
D, Y	French A-1 494 438 (CALGON CORP.) * Claims 1,4 *	1-11	C 08 F 226/02 B 01 D 17/05 C 02 F 1/54
Y	Swiss A-431 994 (BASF AG) * Claim *	1-11	
			SUBJECT AREAS SEARCHED (Int. Cl. ⁴)
			C 08 F
This search report was produced for all the patent claims			
Search site THE HAGUE		Final date of the search January 18 1988	Examiner C. L. M. CAUWENBERG
CATEGORIES OF DOCUMENTS LISTED			
X: of special importance considered alone Y: of special importance in conjunction with another publication in the same category A: technological background O: non-written disclosure P: intermediate literature		T: theories or principles underlying the invention E: older patent document published only on or after the date of the application D: document listed in the application L: document listed for other reasons &: member of the same patent family, agreeing document	

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WATER-SOLUBLE QUATERNARY POLYAMMONIUM SALTS, PROCESS FOR
THEIR PREPARATION AND THEIR USE

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ABSTRACT:

Novel water-soluble quaternary polyammonium salts based on unsaturated quaternary ammonium salts and in particular poly(dimethyldiallylammonium chloride) (poly-DMDAAC) which comprise from 10 to 100 % by weight of highly branched polymer having a molecular weight of

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